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	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	GB 1597270	A	19810903	GB 1978-22887	19780526
AB	A Pb-alk. earth metal alloy for battery electrodes contains Ca, Sr, or Ba (0.75 .times. at. wt.)/40-(0.013 .times. at. wt.)/40, Al 0.0001-0.1, Mg 0.005-0.05, and Sn 0.005-<1.0%. Thus, 1.4-cm-diam rods, manufd. by addn. of Al 0.01, Ca 0.085, Mg 0.1, and Sn 0.7% to molten Pb at 590.degree. were <u>extruded</u> , cut into 12-cm-long electrodes and <u>annealed 1 wk at 100.degree.</u> . The electrodes were used as anodes in corrosion tests for 4 wk at 30.degree. in 5M H2SO4 satd. with N at 1500 mV. The electrode wt. loss was 85 mg/cm2 and tensile strength 6.70 kg/mm2.				

PATENT SPECIFICATION

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(54) LEAD ALLOYS

(71) We, CHLORIDE GROUP LIMITED, a Company registered under the Laws of England, of 52, Grosvenor Gardens, London, SW1W 0AU, England and University of Manchester Institute of Science and Technology, a University Institute incorporated under Royal Charter, of Sackville Street, Manchester M60 1QD, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to lead alloys. These are particularly useful in electric storage batteries in particular for use in the production of cast grids or other support structures for the active material of the electrodes which may be fabricated for such uses by conventional processes such as rolling. The invention is also applicable to electrodes for use in electrolysis cells.

The alloys are also applicable to electrodes in electrolysis cells for producing chemicals, electrowinning and electrorefining of metals, plating baths, to sheathing and cladding to protect articles such as cable and chemical plant and can be fabricated for such uses by conventional processes such as casting, extrusion and rolling.

The specification of British Patent No. 712798 discloses lead calcium and lead tin calcium alloys containing aluminium as an antidrossing agent. The presence of aluminium reduces the oxidation rate of the bulk of the molten metal and minimizes the loss of alloying element.

This earlier specification discloses an alloy containing 0.08% by weight calcium, 1.5% by weight tin, 0.05% by weight aluminium and 98.37% by weight lead. It also teaches that alloys having 0.03% to 0.1% calcium, 1% to 2% by weight tin, 0.01% to 0.01% aluminium, balance being lead and impurities, have superior properties. We have found however that at calcium contents below 0.075% the material is insufficiently hard within acceptable periods of time to be mechanically trimmed and in addition the corrosion of the alloy is greater as the tin content increases above 1%.

Lead-tin-calcium alloys have many excellent properties for use in electric storage battery electrodes but they suffer from a reluctance to recharge and this is referred to as poor rechargeability.

We have found that by the use of selected proportions of magnesium and aluminium, alloys having improved charge acceptance on cycling are obtained.

Thus according to one aspect of the present invention a lead-alkaline earth metal alloy comprises 0.075A/40 % to 0.13A/40 % by weight alkaline earth metal preferably 0.08A/40 % to 0.09A/40 % alkaline earth metal, preferably 0.005% to 0.99% by weight and more preferably 0.1% to 0.8% and especially 0.4% to 0.7% tin, 0.0001% to 0.1%, more preferably 0.0005% to 0.05%, e.g. 0.005% to 0.01% aluminium, 0.005% to 0.05% preferably 0.007% to 0.025% more especially 0.008 to 0.02% by weight magnesium, the balance being lead and impurities, the alkaline earth metal being calcium, strontium or barium and A being the atomic weight of the alkaline earth metal.

Alloys of this defined composition are very suitable for casting into the shape of current

conducting grids for lead acid electric storage batteries. The invention also extends to grids made from such alloys.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

Examples 1-12

12 alloys were made up by adding calcium, magnesium and aluminium (except in Examples 1-4) simultaneously to molten lead at 590°C. Tin was then added. The compositions of the additions to the melt are given in Table 1.

TABLE 1

Example	Calcium	Tin	Magnesium	Aluminium
1	0.085	0.7	0.0004	0
2	0.085	0.7	0.005	0
3	0.085	0.7	0.02	0
4	0.085	0.7	0.10	0
5	0.085	0.7	0.0004	0.005
6	0.085	0.7	0.005	0.005
7	0.085	0.7	0.02	0.005
8	0.085	0.7	0.10	0.005
9	0.085	0.7	0.0004	0.01
10	0.085	0.7	0.005	0.01
11	0.085	0.7	0.02	0.01
12	0.085	0.7	0.10	0.01

The alloys were cast into a mould to produce 1.40 cm diameter rods for subsequent extrusion.

The cast bars were cut into 6 cm lengths before fitting into a preheated extrusion die. The die was electrically heated by a split ring heater to 150°C prior to extrusion. Pressure was applied to the extrusion die after placing it between the plattens of an Ajax metallurgical mounting press. The extruded rod was supported as it emerged from the die by a 100 cm long narrow diameter tube to prevent 'kinking'. The diameter of the extruded rod was 2.5 mm. Electrodes 12 cm long were cut from the rod and annealed at 100°C for one week. Screened copper cable 0.7mm diameter was soldered to the electrode for electrical connection. A predetermined length of 5.5 cm was measured on the electrode and the remainder was protected from corrosion attack by epoxy resin cast inside a 6 mm diameter glass tube containing the screened wire. The wire was further protected from attack by electrolyte by polythene tubing fitted tightly over the glass tubing. The electrodes were used for anodic weight loss studies, the results of which are given in Table 2.

The corrosion tests of Table 2 were carried out at 30°C in 5M sulphuric acid saturated with nitrogen gas, at a constant potential of 1500 mV against a mercury/mercurous sulphate reference electrode.

The potentiostatic corrosion tests involved electrolysis for 4 weeks with the weighed samples (W1) as the anode. The sample electrodes at the end of the corrosion test were withdrawn, washed with water, then acetone and dried in a stream of warm air. These electrodes then had the corrosion products removed by immersion at ambient temperature

for $\frac{1}{2}$ hour in a strip solution prepared from:

	Hydrazine Dihydrochloride	100g	
5	Ammonium Acetate	150g	5
	Glacial Acetic Acid	40g	
10	Water	1 Litre.	10

The stripped samples were then washed, dried and reweighed, W2. The weight loss quoted (W1-W2) was then converted and expressed as mg/cm^2 .

TABLE 2

Example	Anodic weight loss mg/cm^2 at 1500 mV and 30°C after 4 weeks. (average of two results)	Tensile strength Kg/mm^2 (1)
1	13	4.95
2	31	5.15
3	65	5.95
4	182	6.35
5	31	5.10
6	45	5.75
7	58	6.05
8	214	6.75
9	23	5.10
10	37	5.75
11	35	6.05
12	85	6.70

(1) Measured on a 2" gauge length sample of 0.5 inch diameter cast specimen at a straining rate of 6mm/minute.

It will be observed that the alloys (Examples 1, 5 and 9) having a low magnesium content have an inferior strength, whilst those (Examples 4, 8 and 12) having high magnesium content have an inferior corrosion resistance.

Extruded rods of Example 1 and Example 11 of 0.1 inches diameter were then made the anode in 1.280 sp. gravity sulphuric acid and subjected to 1.5 volts for 1.5 hours, the voltage was then reduced to 1.0 volts for 10 minutes and then the 1.5 volts potential reapplied for 1.5 hours, the current being measured continuously. This cycle was repeated 100 times the peak current value observed when the potential is raised again to 1.5 volts was plotted against the cycle number. The current was significantly higher at each cycle for Example 11 than was that for Example 1.

As mentioned above, the alloy of this invention can be converted into supports for the electrodes of lead acid cells either by casting in a mould defining a grid or by cold wrought procedures. When these latter procedures are to be used, the alloy may be continuously cast as a sheet and is then preferably immediately rolled to a sheet once it has solidified or it may be given additional cooling so that it is rolled at about ambient temperature. The rolling can conveniently be carried out continuously, e.g. on the output from a chilled roll continuous sheet casting machine. Thus the rolling may be carried out within less than one minute, e.g. less than ten minutes and certainly less than one hour, from the moment the metal has solidified. This procedure has a desirable effect on the age hardening and strength properties of the alloy.

The sheet may be rolled so as to reduce its thickness to an amount of at least a half i.e. a reduction ratio of at least 2, and preferably at least 4, e.g. in the range of 2 to 20 or 4 to 10.

In the case of supports for the electrodes of lead acid cells the rolled sheet can then be punched out to the desired shape or preferably slit in rows of short spaced apart slits and then pulled either lengthwise or preferably across the length of the strip continuously to form an expanded metal mesh, in this case the rows of slits being along the length of the strip. This expanded mesh is then used as the electrode support and may be pasted with active material in conventional manner.

WHAT WE CLAIM IS:-

1. A lead-alkaline earth metal alloy which comprises 0.075A/40 % to 0.13A/40 % by weight alkaline earth metal, 0.0001% to 0.1% aluminium, 0.005 to 0.05% by weight magnesium, the balance being lead and impurities, the alkaline earth metal being calcium, strontium or barium and A being the atomic weight of the alkaline earth metal. 5
2. A lead calcium alloy which comprises 0.075% to 0.13% by weight calcium, 0.001% to 0.1% aluminium, 0.005% to 0.05% by weight magnesium, the balance being lead and impurities.
3. An alloy as claimed in Claim 1 or Claim 2 which includes 0.08A/40 to 0.09A/40 % by weight alkaline earth metal. 10
4. An alloy as claimed in Claim 1, 2, or 3 which includes 0.005 up to less than 1.0% by weight of tin.
5. An alloy as claimed in Claim 4 which includes 0.4% to 0.7% by weight of tin.
6. An alloy as claimed in Claim 1, 2, 3, 4, or 5 which includes 0.0005% to 0.01% by weight of aluminium. 15
7. An alloy as claimed in anyone of Claims 1 to 6 which includes 0.008% to 0.02% by weight magnesium.
8. An alloy as claimed in Claim 1 substantially as specifically described herein with reference to any one of Examples 6, 7, 10 and 11.
9. An electric storage battery incorporating electrode supports made from an alloy as claimed in any of Claims 1-8. 20

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